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Australian Journal of Basic and Applied Sciences

Published: 02/06/2016

Publisher's PDF, also known as Version of record

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Dyfyniad o'r fersiwn a gyhoeddwyd / Citation for published version (APA):

Mabrook, M. (2016). Effect of annealing on P3HT:IC70BA organicsolar cell devices. *Australian Journal of Basic and Applied Sciences*, 69-73.

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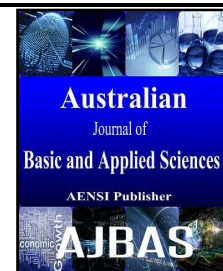
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AUSTRALIAN JOURNAL OF BASIC AND APPLIED SCIENCES

ISSN:1991-8178 EISSN: 2309-8414
Journal home page: www.ajbasweb.com



Effect of annealing on P3HT:IC70BA organicsolar cell devices

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ARTICLE INFO

Article history:

Received 3 April 2016

Accepted 21 May 2016

Published 2 June 2016

Keywords:

Organic solar cell

Indene-C70 bisadduct(IC70BA)

Annealing time

ABSTRACT

A new acceptor material, Indene-C70 bisadduct (ICBA), has reportedly improve the efficiency and the current density. By carefully optimizing annealing temperature and time of annealing high efficiency of 8.4% was achieved. The devices displays huge current density of 38 mA/cm², and high open circuit voltage of 0.6 V.

INTRODUCTION

As sources of alternative energy are increasingly recognized to be more important in the 21st century, solar energy holds a special place as the only energy source that could single-handedly meet the ever-growing world energy demand. Interest in thin-film photovoltaic technologies has grown out of the desire to find inexpensive and readily deployable solar technologies (Petr, P., 2013; Razykov, T.M., *et al.*, 2011; Devabhaktuni, V., M. Alam, 2013; Avrutin, V., *et al.*, 2011; Jacobson, M.Z., M.A. Delucchi, 2011; Armaroli, N., V. Balzani, 2011; Schlenker, C.W., M.E. Thompson, 2012; Jäger-Waldau, 2011; Po, R., *et al.*, 2010; Wangqiao Chen, *et al.*, 2014). Organic solar cells (OSCs) have become one of the most active research areas due to their promising advantages, such as simple structure, clean and renewable energy source, low cost, lightweight, and mechanical flexibility. Normally, an OSC consists of photoactive blend layer (this layer is typically made of conjugated polymers as donors and fullerene derivatives or other molecules as acceptors), which is sandwiched between a transparent indium tin-oxide (ITO) electrode and a low work function metal electrode (Ma, W.L., *et al.*, 2005; Li, G., *et al.*, 2005; Moule, A.J., K. Meerholz, 2009). Great efforts have been devoted to modulate the properties of the bulk heterojunction (BHJ) layers in PSC devices in the past decades. Several molecular design strategies have been successfully used to modulate absorption spectra, bandgaps, and molecular energy levels of the active-layer materials, resulting in significant improvements in the photovoltaic performance of PSC devices (Ma, W.L., *et al.*, 2005; Li, G., *et al.*, 2005; Moule, A.J., K. Meerholz, 2009; Ai, L., *et al.*, 2015; Li, Y.F., 2012; Dou, L.T., *et al.*, 2013; Liu, S.J., *et al.*, 2013; Zhang, M.J., *et al.*, 2013; Liao, S.H., *et al.*, 2013). Annealing treatments result in large scale phase separation of the conjugated polymer and the fullerene material and the initial favorable (intimately mixed) morphology is (quickly) lost (Sabine Bertho, *et al.*, 2013; Yang, X., *et al.*, 2004; Yang, X., *et al.*, 2004). The C60 derivative PCBM is the most widely used electron acceptor material in

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ToCite This Article: Mervat K., M.F. Mabrook, Bushrah A. Hassan., Effect of annealing on P3HT:IC70BA organic solar cell devices. *Aust. J. Basic & Appl. Sci.*, 10(10): 69-73, 2016

PSCs. However C70 derivatives exhibit better absorption than those of C60. Replacing C60 derivatives with C70 derivatives often enhances photocurrent by around 10%. Another important approach for improving PSC performance is by replacing the conventional acceptor PCBM with a new soluble C60 derivative (ICBA), the lowest unoccupied molecular orbital (LUMO) energy level of which is 0.17 eV higher than that of PCBM; this approach leads to higher open-circuit voltages and enhanced power conversion efficiencies (Chunjun Lian *et al.*, 2014; He, Y.J., *et al.*, 2010; Cheng, F., *et al.*, 2013). We review the progress on the modeling and simulation of BHJ PSCs. A comprehensive and intuitive discussion of device performance is provided to help further endeavors to ward device optimization. In the second section, a brief review on the development optical and electrical models is given. The simulation of a conventional PSC is presented with a basic model in the third section, and key factors that affect the device performance, specifically, the photoabsorption, quantum efficiency, short circuit current (I_{sc}), fill factor (FF), and open circuit voltage (V_{oc}) of the device, are analyzed and discussed. Simulations of semitransparent PSCs and large-area PSCs are also performed and discussed. Results are compared with the experimental data from related works and discussed accordingly. Finally, a conclusion is provided in the fourth section.

Experiment:

OPVs were fabricated using pre-patterned ITO-coated glass substrate. Prior to the use, the substrate was cleaned in ultrasonic using 20% Decon90, deionized water, isopropanol, and acetone in the clean room, and later dried with N₂ compressor. All cleaned substrates were treated with O₂ plasma treatment for 25 min. The solution for hole transporter PEDOT:PSS was spin-coated at 5000 rpm for 40 s onto the cleaned substrates and annealed at 140 °C for 10 min. The photoactive layer P3HT:ICBA (1:1) was dissolved in Chlorobenzene with a concentration of 15 mg/ml and was spin-coated at 1500 rpm for 35 s in the glove box and subsequently annealed at 130 °C, 150 °C, 170 °C for 45, respectively, and then with different times for annealing with other devices. Later, TiO₂ solution was spin-coated at 4000 rpm for 25 s onto the photoactive layer and annealed at 75 °C for 20 min. To complete the device, 120 nm thick Al was thermally evaporated at rate 1 Å/s through a shadow mask at a base pressure of 10⁻⁶ mbar. The active area of the complete devices is 0.12 cm². Devices were tested under AM 1.5 illumination with an intensity of 100 mW/cm² simulator at room temperature in nitrogen glove box. The idealized device configuration is depicted in Fig. 1.

RESULTS AND DISCUSSION

Fig. 2. Presents J-V characteristics for devices with P3HT/ICBA films annealed at different temperatures between 130 °C and 170 °C (the device without any annealing is also included for comparison). The corresponding values of V_{oc} , J_{sc} , FF and η for these devices are summarized in table 1. The device without any thermal treatment delivers a low η of 3.8% with V_{oc} of 0.57 V, and J_{sc} of 21 mA/cm², and FF of 31%. Thermal annealing at 130 °C increased η rapidly to 8.2% with significant increasing in V_{oc} , J_{sc} and FF (0.65 V, 35 mA/cm² and 36%, respectively). When the annealing temperature goes up to 150 °C, η and FF are slightly decrease but no changes are noticed in other parameters. The highest η of 9% was achieved when the annealing temperature is increased to 170 °C (J_{sc} and FF are also the highest at this temperature). Hui Li *et al.* (Hui Li, *et al.*, 2012) found that higher annealing temperature to 180 °C degrades device performance, resulting in much decreased J_{sc} , which drags down PCE as a result. The sudden drop of J_{sc} might be caused by the decrease in molecular weight or even changes of chemical structures (Gritsenko, K.P. and A.M. Krasovsky, 2003; Kovacic, P., *et al.*, 2011). Annealing induced performance improvement can be generally attributed to enhanced exciton dissociation at donor/acceptor interface: annealing can strengthen the donor-acceptor molecular interaction, and thereby promote carrier exchange process, making charge separation more efficient. Besides, annealing could also increase carrier mobility, owing to the improved qualities of both donor and acceptor materials and their interface: thermal annealing could drive out remnant solvent in as-cast film, and enable better P3HT crystallization in the film (through extended conjugation lengths and interchain interactions). But here we believe that the improvement should be directly due to the strengthened inter-diffusion of ICBA into P3HT, which transforms the original bilayer-like structure into a BHJ structure.

Fig. 2(b) displays J-V characteristics of devices with different annealing time at 170 °C, in which detailed device parameters are inserted. It shows that when the annealing time is 30 min, the performance increases a lot in comparison with the device without any thermal treatment. Longer annealing of 45 min further increases the device performance. Further longer annealing time treatment, however, cannot improve device performance anymore. This can be understood in this way: the optimal mixture and high-quality donor/acceptor interface are already formed during the initial 45 min annealing treatment, further annealing can no longer do any favor to the interface, if not damage the interface, and thereby cannot improve the device performance.

UV- visible absorbance curves of the devices with as-cast films and films annealed at different temperatures and different times are shown in Fig. 3(a) and (b) respectively. The strong absorption feature near 450 nm for all samples can be ascribed to the interchain vibrational absorption induced by the strong interchain interaction in

theordered P3HT crystalline regions in the films (Kovacik, P., *et al.*, 2011). It is seen that devices with annealedfilms exhibit higher absorbance than the device with as-cast films. The highestabsorbance value belongs to the device annealed at 170 °C for 45 min. consistent withthe observation of largest Jsc in Table I, which should be attributed to the enhancedexciton dissociation efficiency at the donor/acceptor interface. The dependence ofabsorbance on annealing temperature and time has the same tendency with that of Jsc. Which are all manipulated by the quality of the solar cell diode.

Besides the above-mentioned parameters, the morphology of the photoactive layerplays a key role in the photovoltaic performance of PSCs. The surface morphology withor without annealing treatment via tapping-mode atomic force microscopy (AFM) isdirectly examined. The AFM topography images are shown in Fig. 4.

However, thermal annealing at 150 °C and 170 °C greatly enhanced the phaseseparation in the P3HT:IC70BA blend.

The lack of such structures in the unheated P3HT:IC70BA films may account forthe improvement of the device performance before thermally annealing. Nevertheless,the lack of the ability for the P3HT:IC70BA to phase separation sufficiently couldalso limit its performance because the preferential interaction between ICBA and P3HTmolecules may interrupt the self-organization of both donor and acceptor moleculesand, hence, lower the effectiveness of the charge transport in the device.

And after appropriate annealing time which was 45 min., IC70BA particlesaggregated to the tens-of-nanometers length domains, thus, forming nanoscale phaseseparation of the blend films. This relatively smooth surface and more ordered structureare beneficial to the charge transport, thus leading to an increase in JSC and VOC, as wellas the device efficiency.

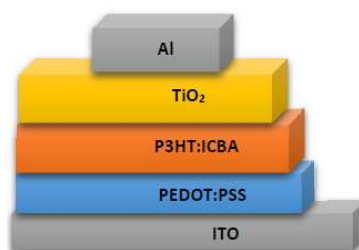


Fig. 1: Idealized device structure

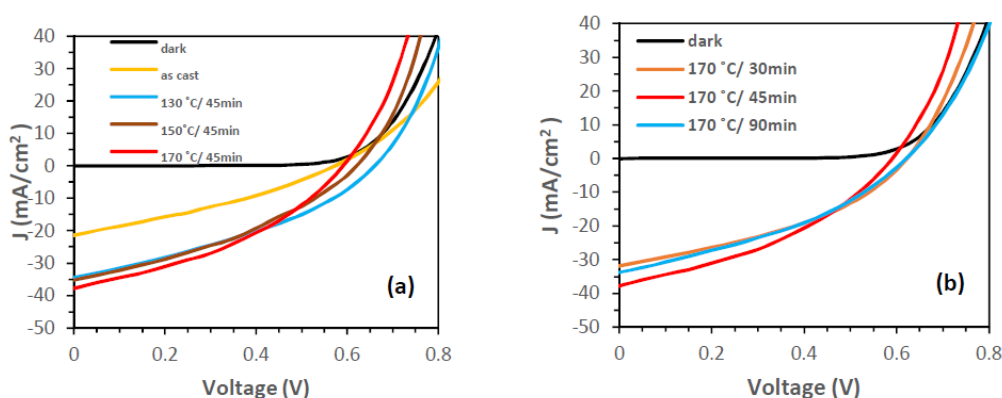


Fig. 2:J-V characteristics depending on(a) annealing temperature. (b) annealingtime.

Table I: Parameters for the devices with as-cast films and films annealed at various temperatures.

Annealing temperature	Voc (V)	Jsc(mA/cm ²)	FF (%)	ηe (%)
As cast	0.57	21	31	3.8
130 °C	0.65	35	36	8.2
150 °C	0.62	35	35	7.8
170 °C	0.6	38	38	8.4

Table II:Parameters for the devices for films annealed at 170°C varioustimes.

170 °C	Voc (V)	Jsc(mA/cm ²)	FF (%)	ηe (%)
30 min.	0.65	31	37	7.6
45 min	0.6	37	38	8.4
90 min	0.65	33	35	7.6

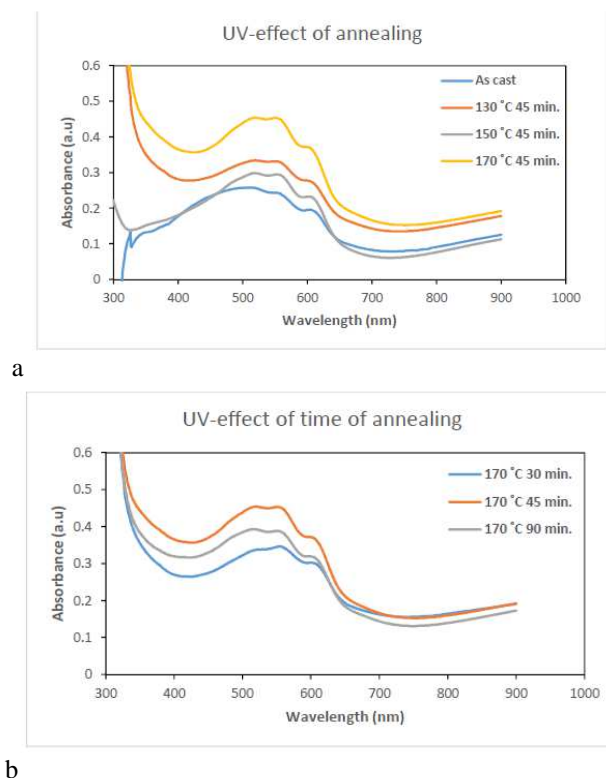


Fig. 3: UV- visible absorbance dependence on: (a) annealing temperature, and (b) annealing time.

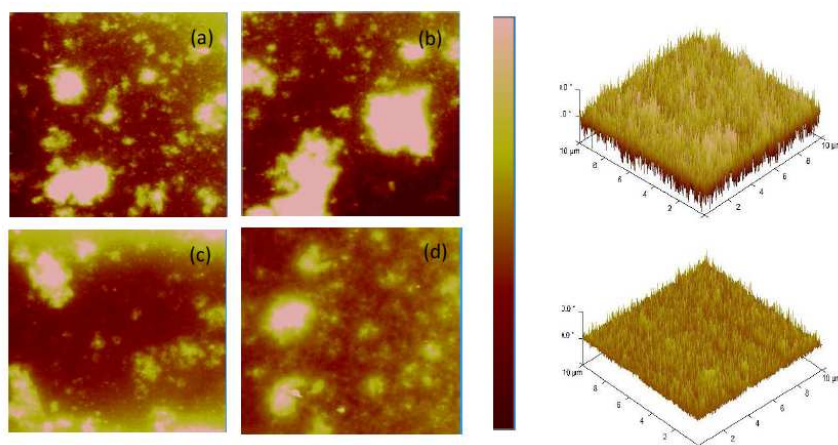


Fig. 4: Tapping-mode Atomic Force Microscopy (AFM) topography image of the blend film of P3HT:ICBA (1:1, w/w); (a) without annealing, (b) with 130 °C annealing temperature, (c) with 150 °C annealing temperature, (d) with 170 °C annealing temperature, (e) three-dimensional (3D) surface plot without annealing treatment, and (f) 3D surface plot with 170 °C annealing temperature. (All image sizes are 10 μm \times 10 μm).

Conclusion:

In summary, a high efficiency of 8.4%, and a huge current density of 38 mA/cm^2 , with a high open circuit voltage of 0.6 V was achieved for P3HT:ICBA polymer solar cell. The dependence of device performance on annealing temperature and time processes are analyzed and discussed. The optimum annealing temperature and time were 170 °C and 45 min. respectively.

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